ZORFLEX ADSORPTION OF ATRAZINE IN DRINKING WATER

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Abstract
Different types of carbon fibres cloths made of 100 % activated carbon were tested in water purification experiments. The atrazine removal efficiencies were studied on carbon cloths named Zorflex® ACC with a specific area of 1000-2000 m^2 /g. The experiments were performed in millipore water and real drinking water samples. The atrazine concentrations were chosen on two levels 1 µg/L and 1 mg/L. In order to improve the adsorption efficiency, the fibres were treated with different solutions. Some of the carbon cloths were regenerated with methanol and used again. A little less than 10 mg of atrazine per 1 g C-cloth was adsorbed. It could beattributed to the fact that in the real water some ions express higher binding affinity to the fibers. Since atrazine was in low concentrations, the removal of atrazine did not depend on methanol concentration.

Keywords: *Atrazine, carbon cloths, thermodynamics*

Introduction
Atrazine is a well-known persistent herbicide and endocrine disruptor for mammals [1]. According to the monitoring report [2] from our government the concentrations of atrazine are still above 0,1 µg/L in Slovene drinking water sources. Although, the adsorption of atrazine has been extensively studied, very little is known about adsorption onto activated carbon cloths. Different types were studied for nitrate removal. However, some studies of atrazine removal using carbon cloths were found. Activated carbon cloths were firstly used for pesticide removal [3] and later also for nitrate removal [4] The efficiency of pesticide removal was increased if the carbon cloths were modified with treatment in hot millipore water at 60°C. [3] The modification with acid solution turned to be more appropriate for nitrate removal [5]. Carbon clothes were successfully used for some pharmaceuticals removal [6].
To the best of our knowledge, thermodynamics of atrazine during the adsorption on carbon cloths was not studied yet. However, it was studied by using nanotubes for atrazine removal. The influence of oxygen was studied. Gibbs energy was negative which meant spontaneous reaction of atrazine on nanotubes [7].
In the present work the effects of functional groups on the adsorption efficiency of atrazine by carbon cloth was investigated. For the modification of surface functional groups and porous structures, the carbon cloths were chemically etched in different solutions, such as methanol and hot millipore water under inert conditions. The thermodynamic and kinetics of atrazine removal on carbon cloths were studied.

Experimental
ZORFLEX® ACC are microporous cloths, made of 100 % activated carbon and have large specific surface area of 1000-2000 m^2/g. They are available in knitted (FM30K) or woven fabric (FM70) as presented in Fig 1a and 1b, respectively.

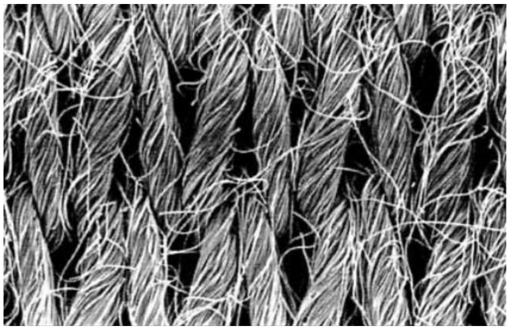
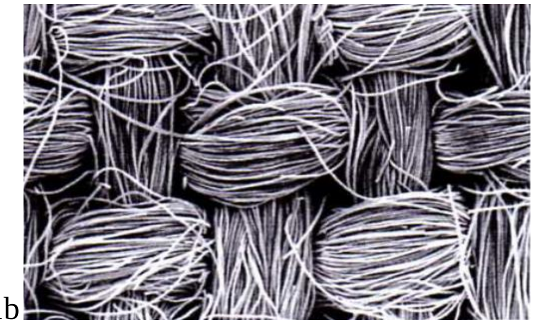
1a  1b 

Figure 1 ACC fibres at 40x magnitude (knitted 1a) and wowen 1b)

Table 1 represents the surface area and thickness of the fibres used.

Table 1: The surface area and thickness of the fibres

Fibre	**FM30K**	**FM70**
Surface area (g/m^2)	110	160
Thickness (mm)	0,4	0,6

Initial carbon cloth treatment and modification

The cloth with the mass of 1 g was placed into a beaker with millipore water for 2 days. Nitrogen gas was bubbled into the cup to avoid possible CO_2 adsorption. The washed carbon cloth modules were then dried under vacuum at 120 ◦C and kept in a desiccator for further uses. For the modification of surface functional groups and porous structures, the carbon cloth was submersed in different solutions. Firstly, cloths were only wetted by water and atrazine adsorption was performed. Secondly, treatment using methanol solution was performed. Thirdly, acid treatment using 15 % H_2O_2 solution was performed. The carbon cloth was then washed with triply distilled deionized water and used. Initial concentration of atrazine was always the same, determined at 1 mg/L and after 2, 5, 20, 40, 60 and 120 mins the concentrations were measured again.

Analyses

Atrazine concentration in water samples was determined following SIST ISO 10695/2000, using LC/MS/MS. Solid phase extraction (SPE) was performed with using cartridges as well as methanol and ethyl acetate as solvents. Bod elute SPE was used which is made of C8 (non-polar).

Adsorption capacity N_f (mg/g) was determined according to Eq. 1:

$$N_f = \frac{V(\gamma_0 - \gamma_s)}{m} \qquad \text{Eq.1}$$

where

γ_0 initial mass concentration (mg/L)

γ_s equilibrium mass concentration (mg/L)

m activated carbon cloth fibre mass (g)

V volume of water solution (L)

To analyse the adsorption rate of atrazine onto carbon cloths, the pseudo second order was evaluated based on experimental results according to Eq.2:

$t/q_t = 1/(k_2.q_{c2}) + t/q_e$ Eq.2

where q_e (mg/g) and q_t (mg/g) are the concentrations of atrazine adsorbed on cloth at equilibrium and at time t, k_2 (g/mg.min) is the rate constant.

Results and discussion

Sorption capacity of atrazine

The results obtained are presented in Fig. 1. The concentrations of atrazine in time dependence for water were done with FM30K cloth. It is seen that already after 40 mins the total removal of atrazine was noticed. The concentrations of atrazine decreased in water for up to 97 %. Desorption of adsorbed atrazine and other ions was performed, however, after the desorption no noticeable differences in atrazine adsorption were noticed.

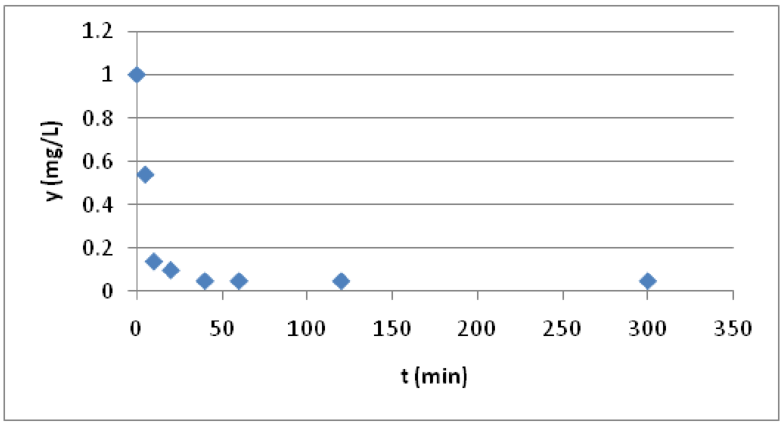


Figure 1. Atrazine removal in dependence of time

The linear regression of the sorption is shown in Fig. 2. The R^2 value close to 1 clearly shows the pseudo second order of reaction.

Effect of temperature was studied on atrazine removal. The standard energy change ΔG^o was calculated as negative value of product of R, T and ln K_o, where constant K_o was determined using a method described by equation 3:

$K_o = a_s/a_e = v_s.c_s/(v_e.c_e)$ Eq. 3

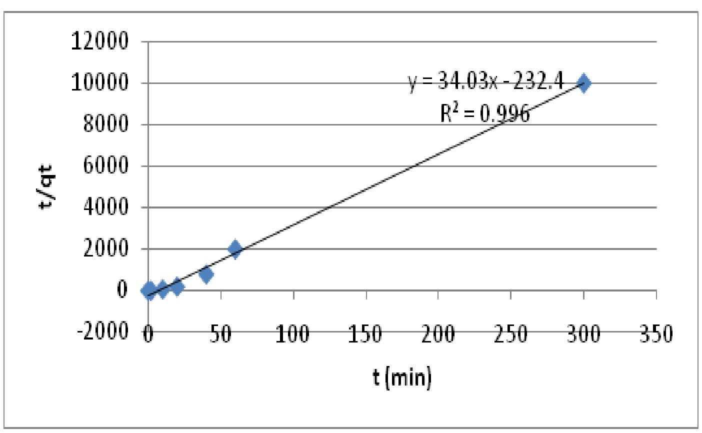


Figure 2. Pseudo second order kinetics of atrazine

Average enthalpy change ΔH^{o} was obtained by Van't Hoff equation:

$$\mathrm{Ln}\ K_o(T_3) - \ln K_o(T_1) = -\Delta H^{o}/R.(1/T_3 - 1/T_1) \qquad \text{Eq. 4}$$

The values ΔG^{o} determined at 295, 303 and 323 C were -0.90 kJ/mol, -1.67 kJ/mol and -1.83 kJ/mol, respectively. All three values are negative, therefore, the adsorption of atrazine is spontaneous. ΔH^{o} was calculated at -11,58 kJ/mol and is negative, which is supported by the observation that the adsorption decreased with increasing temperature.

Conclusions

Carbon cloths designed as "Chemviron Zorflex® ACC" were tested for their adsorption of atrazine in millipore water. Modification with acid or methanol did not affect the removal efficiency. The results showed that atrazine adsorpction follows the pseudo second order kinetics. Gibbs energy was determined to be negative, therefore, the adsorption of atrazine is spontaneous. Average enthalpy was determined at the value of -11,58 kJ/mol.

References

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